3rd NASA NIST Workshop on Nanotube Measurements
Gaithersburg, MD, 27 September 2007

Metallic vs. Semiconducting Single-Walled Carbon Nanotube Separation Using Dielectrophoresis

Manuel J. Mendes, Noe Alvarez, Howard K. Schmidt and Matteo Pasquali

APPLIED PHYSICS PROGRAM,
DEPART. OF CHEMISTRY
DEPART. OF CHEMICAL & BIOMOLECULAR ENGINEERING
CARBON NANOTECHNOLOGY LABORATORY
THE SMALLEY INSTITUTE FOR NANOSCALE SCIENCE & TECHNOLOGY
RICE UNIVERSITY, HOUSTON, TEXAS

OUTLINE

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  - What is dielectrophoresis (DEP)
- THEORETICAL PRINCIPLES
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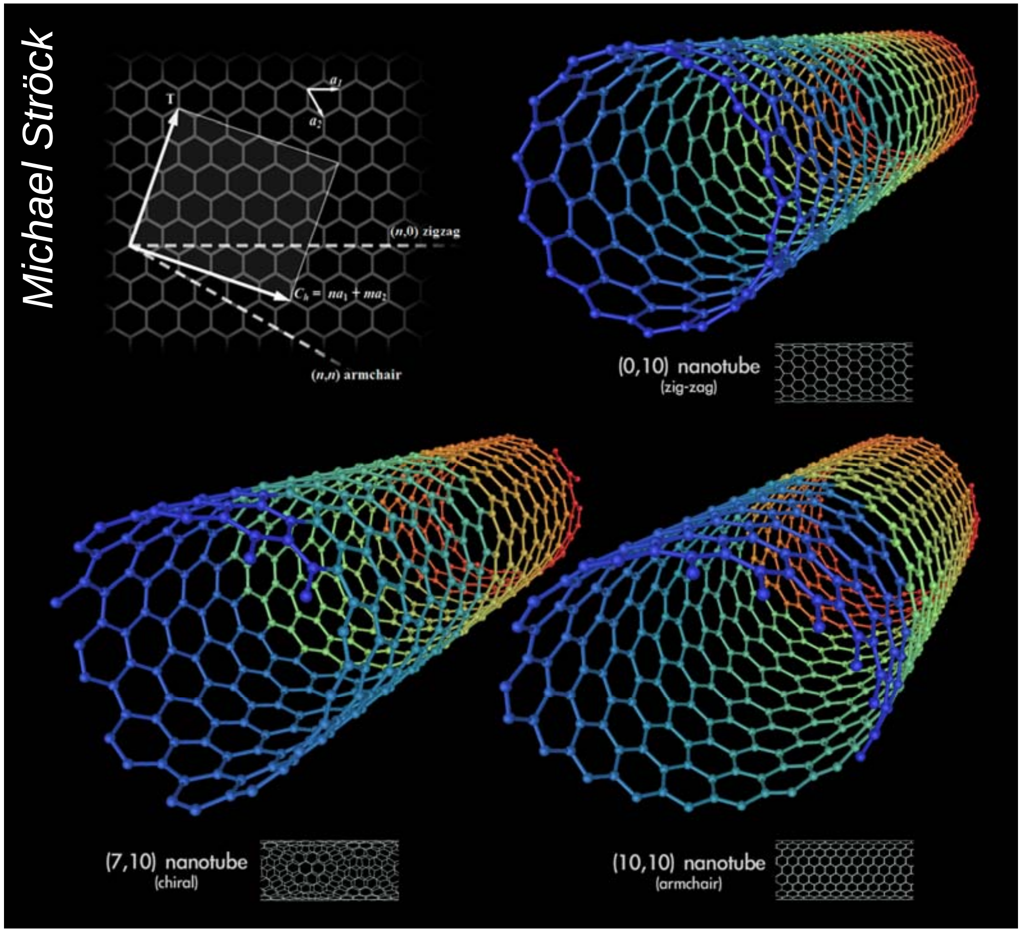
  - Coaxial channel geometry
  - Governing equations: forces & torques
- BROWNIAN DYNAMICS SIMULATIONS
  - Rotational Phase Diagram
  - Device Performance
  - Effect of Ensemble Size
  - Optimization with Simplex Method
- EXPERIMENTAL RESULTS
  - Measuring Type Enrichment
  - Results with Pluronic Decants
  - Studying the Surfactant Effect
  - Mixtures of Anionic and Cationic Surfactants
- CONCLUSIONS
- ACKNOWLEDGEMENTS

SWNT ARE A CLASS OF MOLECULES



Chirality (n,m) identifies the species

(n,0) and (0,m): zig-zag
(n,n): armchair
(n,m): chiral

•Metallic: $n = m$ (bandgap = 0 eV)
•Semi-metallic: $n - m$ is multiple of 3 (“mod 3 tubes,” bandgap ~1-10 meV)
•Semiconducting: $n - m$ is not a multiple of 3 (bandgap ~0.5 - 1.0 eV; HiPco 0.8-1.4 eV)

- Current methods produce mixtures of metallic/semi-metallic (1/3rd) and semiconductors (2/3rd)
- Different diameters, polydisperse length

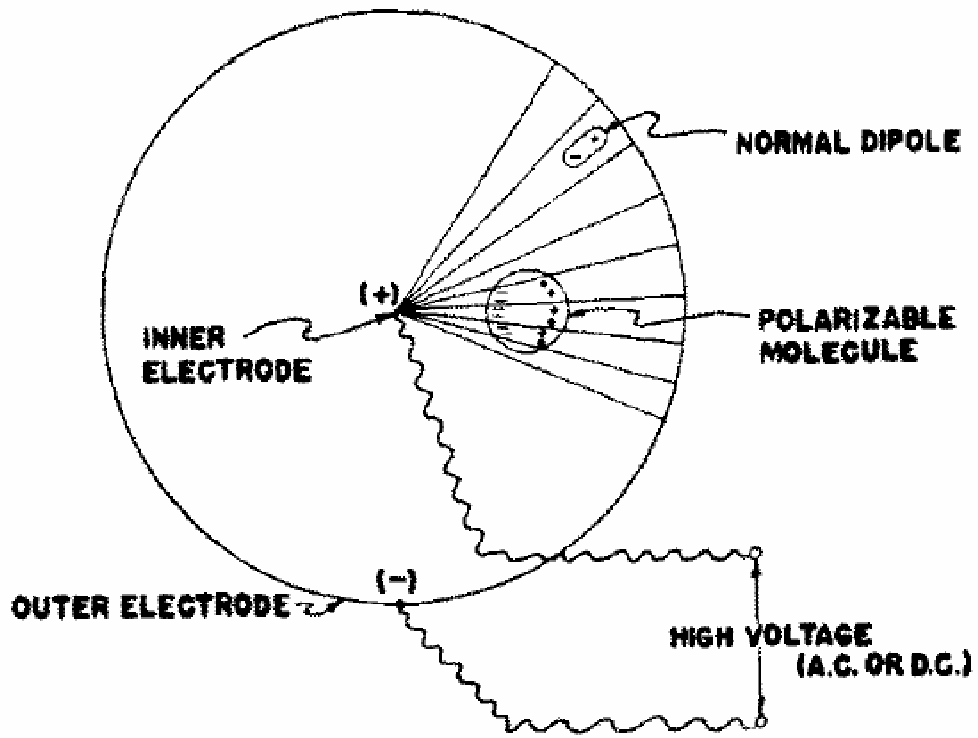
CURRENT TYPE SEPARATION METHODS

- Covalent functionalization – *Strano et al*., Science 2003
- Selective adsorption – *Chattopadhryay et al.,* JACS 2003
- Ion exchange chromatography – *Zheng et al.,* Science 2003
- Selective elimination by electrical breakdown – *Collins et al*., Science 2001
- Density gradient ultracentifugation –*Arnold et al.,* Nature Nanotech. 2006
- **Electrophoresis –** *Heller et al.,* JACS 2004
- **Dielectrophoresis** – *Krupke et al.,* Science 2003

So far, all methods yield small quantities of SWNTs (mg)
Some may be scalable: modeling can help scale-up

WHAT IS DIELECTROPHORESIS (DEP)

- Motion of particles caused by polarization effects in a **Nonuniform Electric Field**



- The direction of motion is independent of the field direction

- For the same field, metallic particles have an higher dipole moment than semiconducting ones

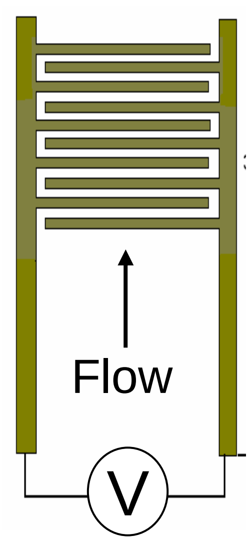
$$\mathbf{F}^{DEP} = \mu \cdot \nabla \mathbf{E}$$

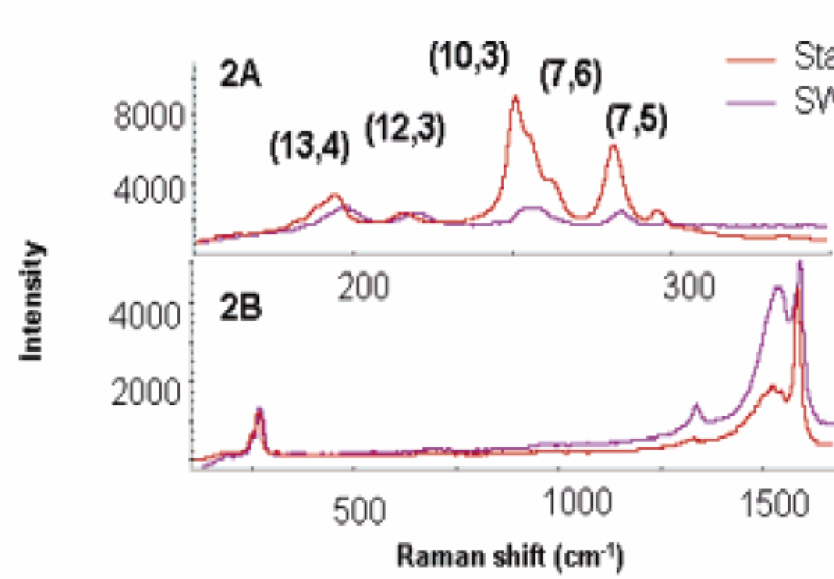
$$\mu \propto \mathbf{E} \longrightarrow \mathbf{F}^{DEP} \propto \nabla \mathbf{E}^2$$

Ref: *Pohl*, J.A.P. 1958

PREVIOUS DEP SEPARATION

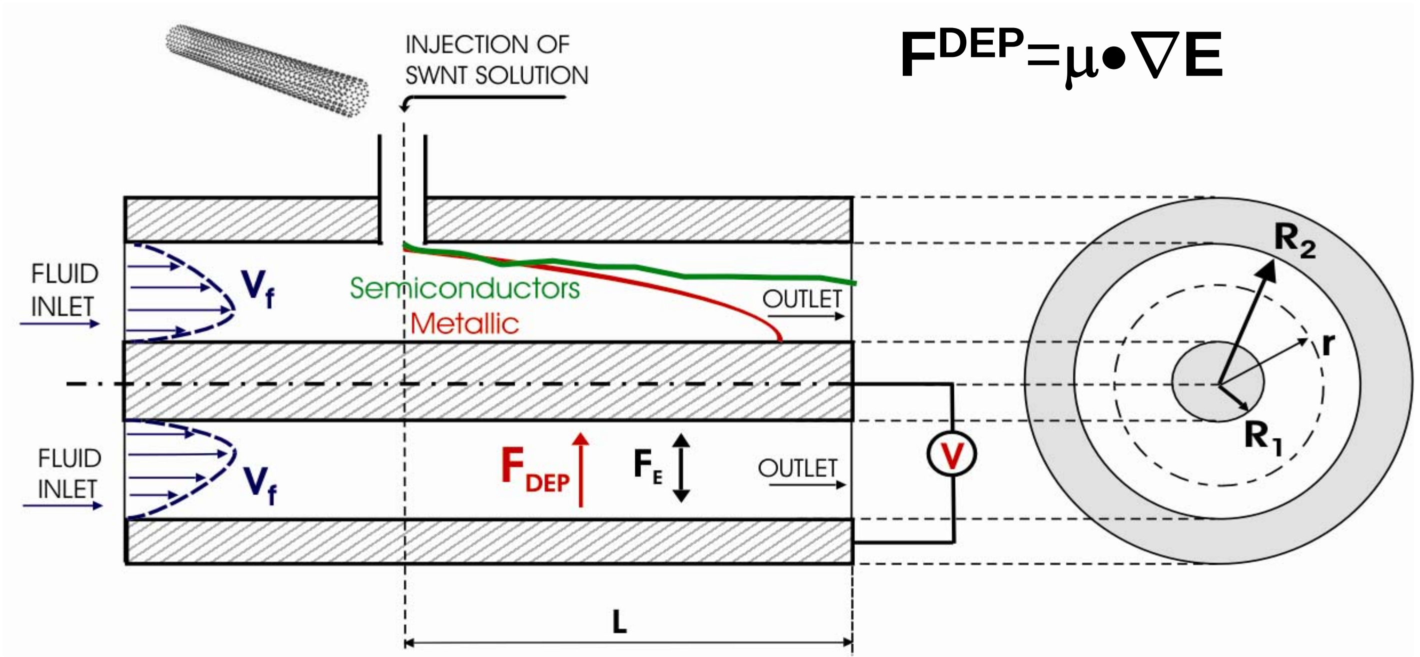
- *Ralph Krupke et al. Science* 2003 – First work on metallic vs. semiconductors DEP separation with a drop of solution placed on an interdigitated electrode array
- *Kim et al.* J. Phys. Chem. B, 2006 (Strano) – Used the same method as *Krupke* but with mixtures of *anionic* and *cationic* surfactants (*main results are shown later*)
- *Haiqing Peng et al.* JACS, 2006 (@ Rice) – Extended Krupke's method for **higher throughput** using *DEP-Field Flow Fractionation (DEP-FFF)*:





Raman spectra collected with lasers:
(A) - 633 nm
(B) - 514 nm

COAXIAL CHANNEL GEOMETRY



$F^{DEP} = \mu \bullet \nabla E$

- **Advantages of Coaxial Geometry:**
  - F^{DEP} scales with $1/r^3$ like in interdigitated electrodes; no regions with $F^{DEP}=0$
  - Analytical expression for flow and DEP fields and forces
  - No need for microfabrication

Spatial Scaling of Electric Forces:

$$\mathbf{F}^{DEP} \propto \nabla \mathbf{E}^2 \propto V_{AC}^2/r^3$$
$$\mathbf{F}^{E} \propto \mathbf{E} \propto V_{DC}/r$$

- A small Electrophoretic force $\mathbf{F}^{\mathbf{E}}$ prevents the *Semiconducting SWNTs* from diffusing to the outer radius R_2, making them remain in solution

SWNTs EQUATIONS MOTION

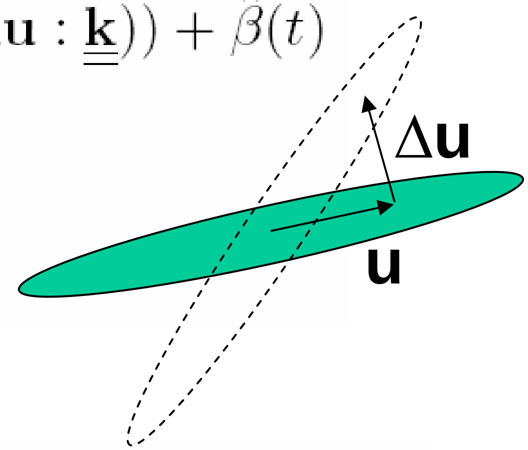
$\boxed{0 = F^{T} + F^{Hydro} + F^{Brown}}$ $F^{T}=F^{DEP}+F^{E}$ $\longrightarrow$ Same for **Torques**

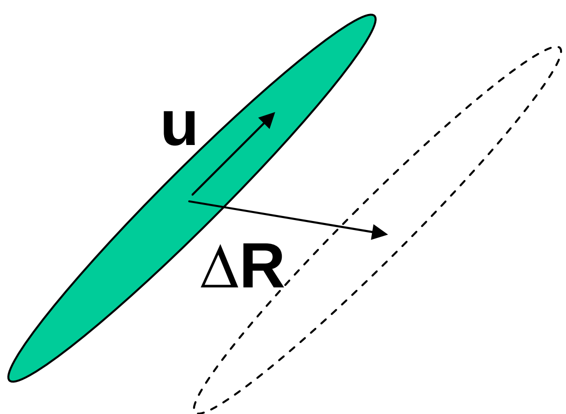
- *Inertia neglected:* small SWNT mass; acceleration time scale (*ps*) << viscous scale
- Brownian forces are important: stochastic differential Eq. – **Brownian Dynamics Algorithm** with Forward Euler scheme to integrate eqs. of motion
- Optimal Parameters for Cylinders radius, Voltage and Flow determined

$$\mathbf{u}(t+\Delta t)-\mathbf{u}(t)=\frac{D^{R}}{K_{B}T}\mathbf{M}_{T}\times\mathbf{u}(t)\Delta t+\Delta t(\underline{\underline{\mathbf{k}}}\cdot\mathbf{u}-\mathbf{u}(\mathbf{uu}:\underline{\underline{\mathbf{k}}}))+\hat{\beta}(t)$$

$$\underline{\underline{\mathbf{k}}}=\nabla\mathbf{v_{f}}$$

$$<\hat{\beta}(t)\hat{\beta}(t)>=2D^{R}(\underline{\underline{\mathbf{I}}}-\mathbf{uu})\Delta t$$



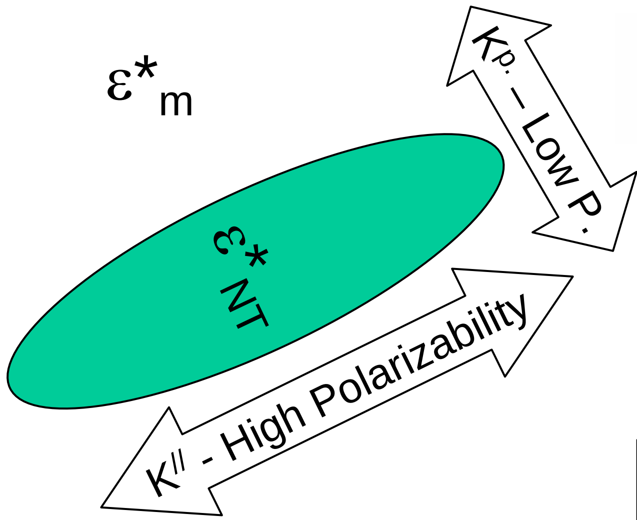


$$\mathbf{R}(t+\Delta t)-\mathbf{R}(t)=\frac{\Delta t}{K_{B}T}\underline{\underline{\mathbf{D}}}\cdot\mathbf{F}_{T}+\mathbf{v}_{f}\Delta t+\mathbf{b}(t)$$

$$<\mathbf{b}(t)\mathbf{b}(t)>=2\underline{\underline{\mathbf{D}}}\Delta t$$

Ref: *Hartmut Lowen,* Phys. Rev. E, 1994

CLAUSIUS-MOSSOTTI FACTOR



$$< \mathbf{M^E} >= V_{NT}\epsilon_m Re\left[K^{//}K^{\perp}\right](L^{\perp} - L^{//})E^2_{RMS}(\mathbf{u}\cdot\mathbf{r})(\mathbf{u}\times\mathbf{r})$$

$$\mathbf{F}^{DEP} = \frac{V_{NT}}{2}\epsilon_m Re\left[K\right]\nabla E^2$$

$$\boxed{K^{\perp,\|} = \frac{\epsilon^*_{NT} - \epsilon^*_m}{\epsilon^*_m + (\epsilon^*_{NT} - \epsilon^*_m)L^{\perp,\|}}}$$

$$\boxed{\epsilon^* = \epsilon - i\frac{\sigma}{2\pi f}}$$

ε* – Dielectric Constant

ε – Permittivity

σ – Conductivity

f - Frequency

- SWNTs modeled as prolate ellipsoids to compute *depolarization factors L*
- For frequencies f ~ MHz, K_M remains constant ($K_M^{//}$~10^4); K_S can change several orders of magnitude
- Separation efficiency is chiefly controlled by the **Polarization ratio** set by selecting f in the MHz range:

$$\boxed{P(f) = Re[K^{\|}_{M}]/Re[K^{\|}_{S}]}$$

Ref: *Ralph Krupke et al.* Nano Lett., 2004

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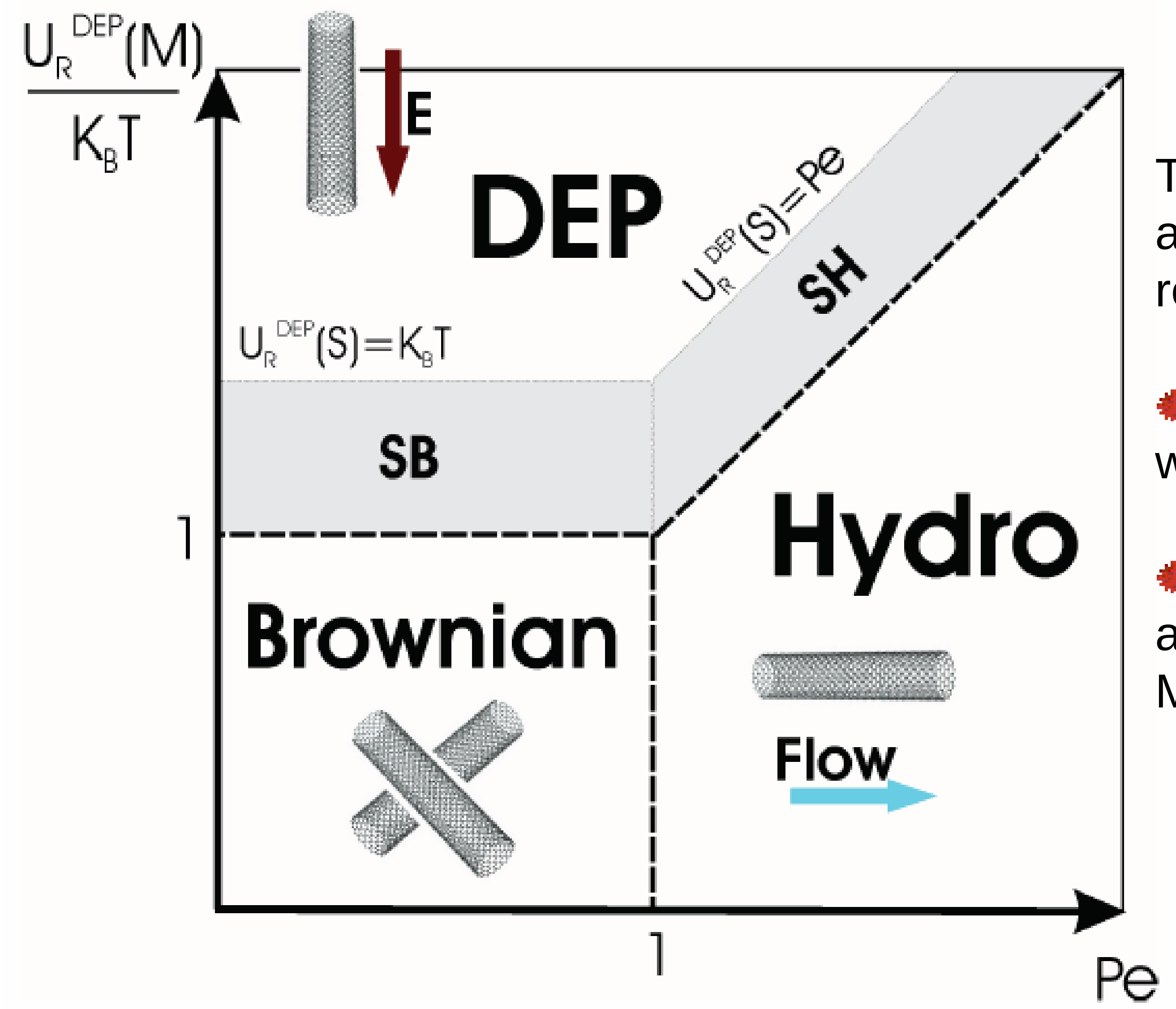
ROTATIONAL PHASE DIAGRAM

$0 = F^{DEP} + F^{Hydro} + F^{Brown}$

$0 = M^{DEP} + M^{Hydro} + M^{Brown}$



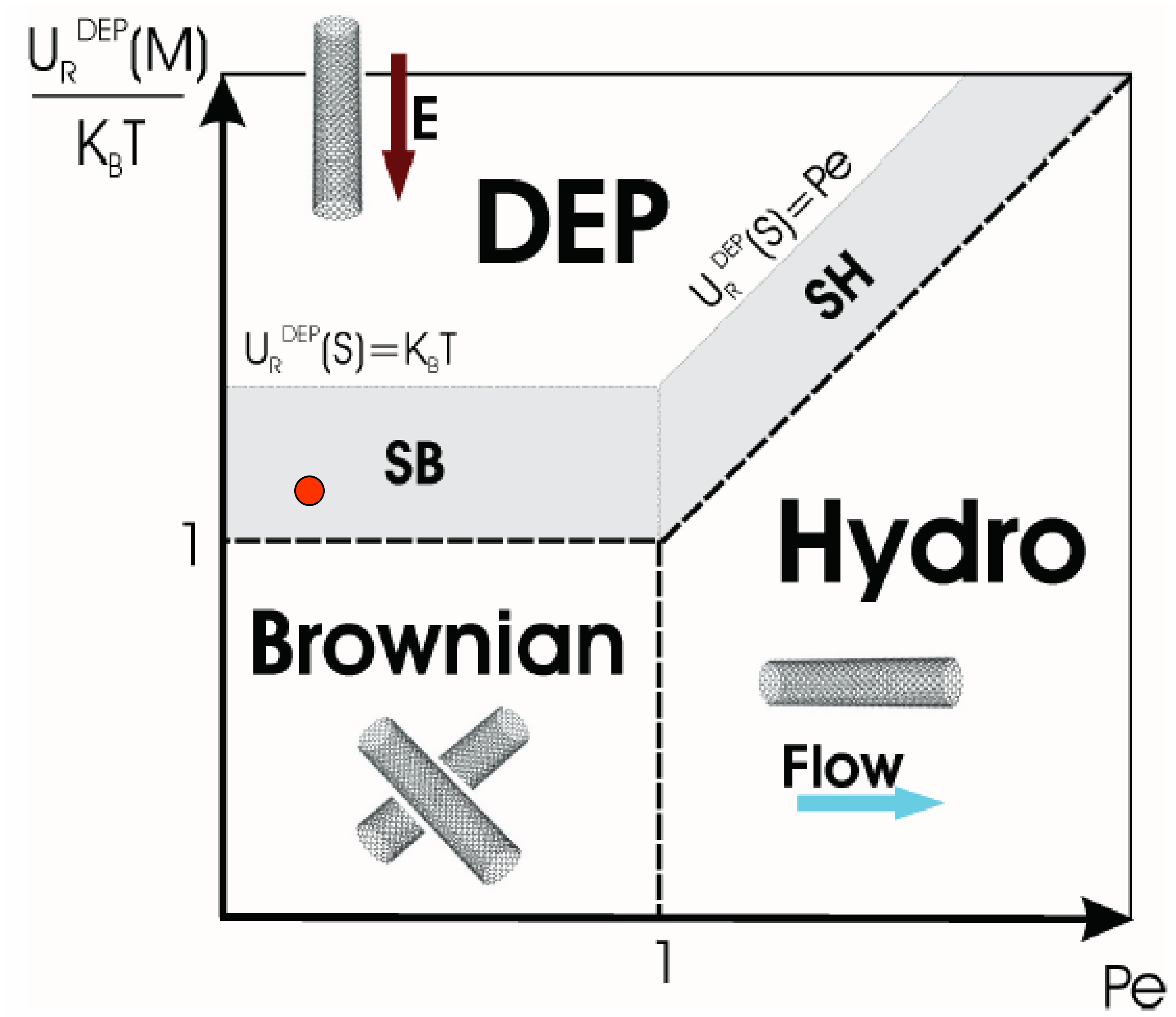
The two shaded areas are the preferential regimes for separation:

- **SB** – Only Metals align with field
- **SH** – Semiconductors align with flow and Metals with field

ROTATIONAL PHASE DIAGRAM

$$0 = F^{DEP} + F^{Hydro} + F^{Brown}$$

$$0 = M^{DEP} + M^{Hydro} + M^{Brown}$$



$$\frac{R_2}{l^p} = 10^3$$

$$\frac{U_R^{DEP}(M, R_2)}{K_B T} = 10$$

$$\frac{T^{DEP}(R_2 \rightarrow R_1)}{T^{BM}(R_2 \rightarrow R_1)} = 0.1$$

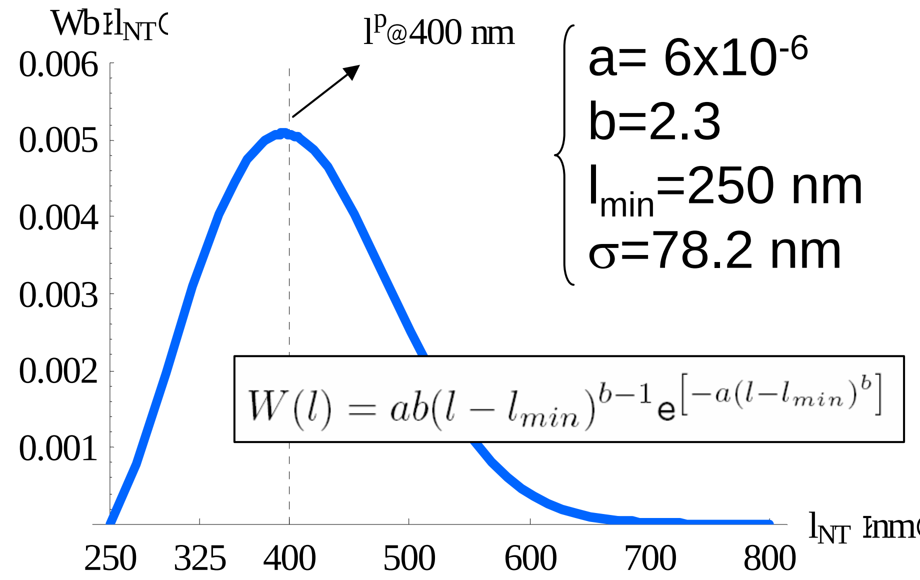
$$Pe(R_1) = \frac{\frac{\partial v_f}{\partial r}\big|_{R_1}}{D^R} = 0.01$$

$$\frac{M_M^{DEP}(R_2)}{M^{Hydro}(R_2)} = 1551.3$$

LENGTH DISTRIBUTION

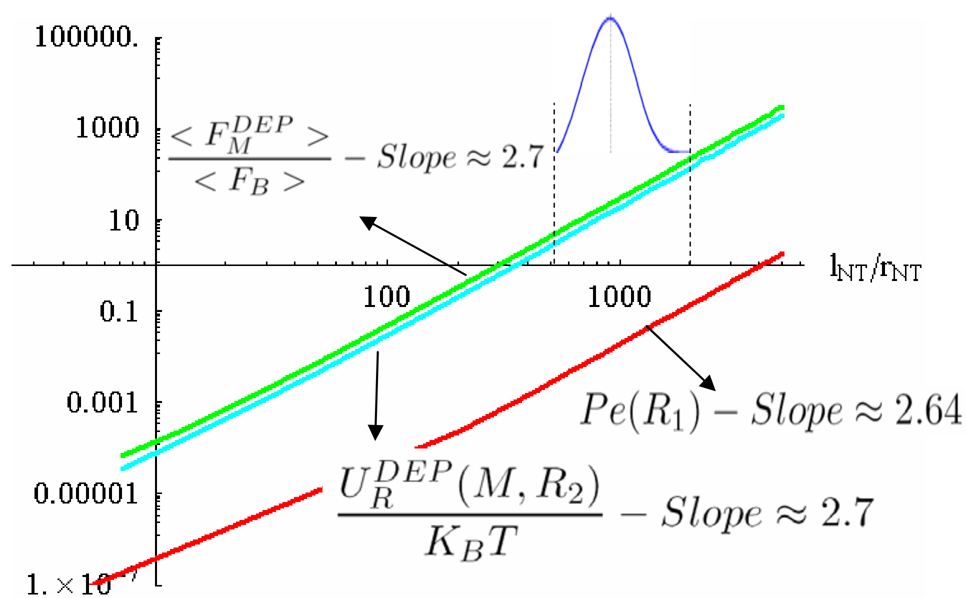
- Fixed uniform radius **r_{NT}=0.5 nm**
- l_{NT} = random number following a **Weibull (W) distribution**
- The parameters for the distribution were chosen so that:

$$\frac{U_R^{DEP}(M, R_2, l_{min})}{K_B T} > 2 \qquad \left(\frac{<l> + 2\sigma}{l_{min}}\right)^{2.7} < 10$$



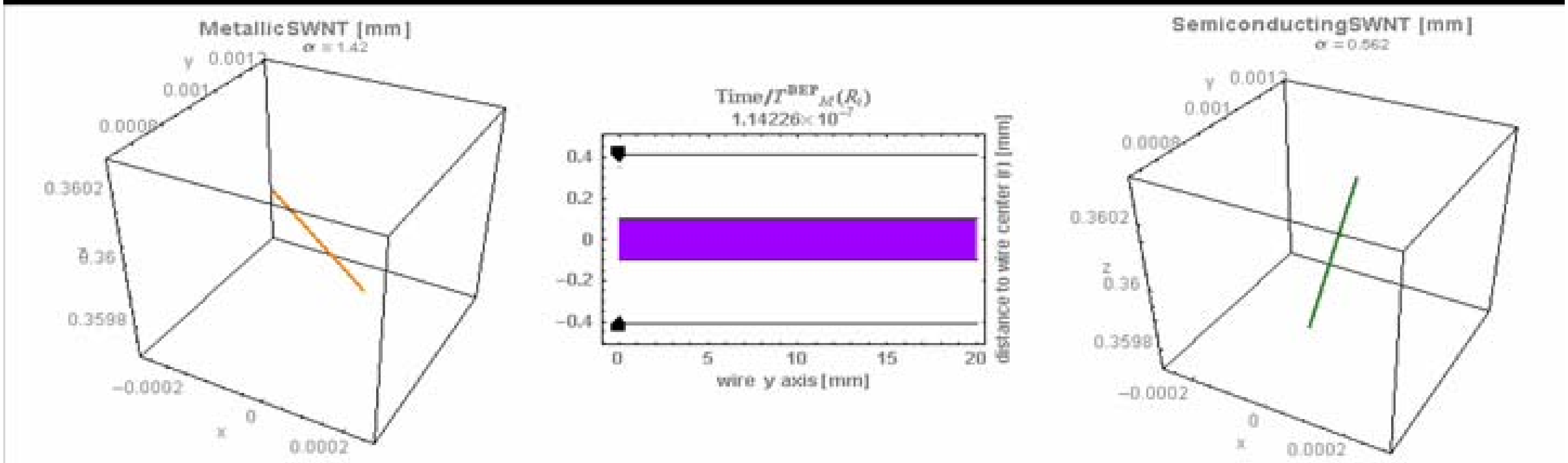
Ref: *Shiren Wang et al.* Nanotechnology, 2003

- Represent length distribution of **HiPco SWNTs** subjected to a <u>length sorting technique</u>: *Becker et al.(NIST)* Adv. Mater. 2007
- In the regime where DEP and Hydro dominate the <u>SWNT alignment</u> is practically length independent



MOTION OF SWNTs IN DEVICE: DEP + EP

Separation trailer with 6 metals (red) and 6 semiconductors (green)



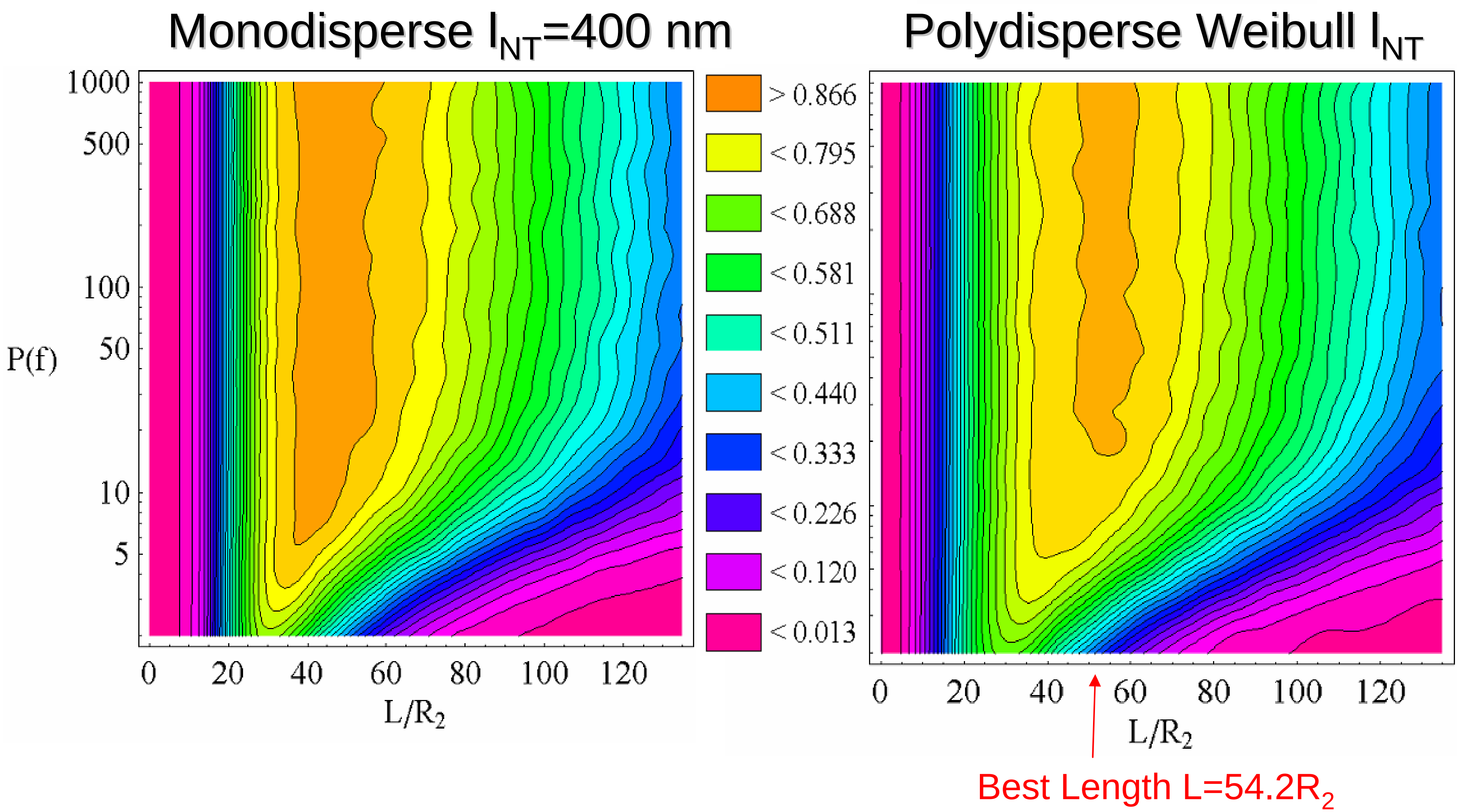
Side boxes show the orientation of one of the SWNTs

S_{MS}=10 , Fixed length l_{NT}=400 nm

DEVICE PERFORMANCE (P): DEP + EP

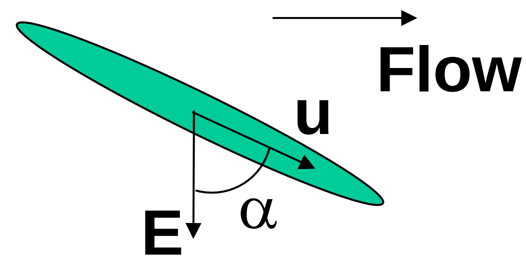
- Independent of initial fraction of injected semiconductors versus injected metals

$$P = \frac{N_M^{col.}}{N_M^{inj.}} \frac{N_S^{sol.}}{N_S^{inj.}}$$

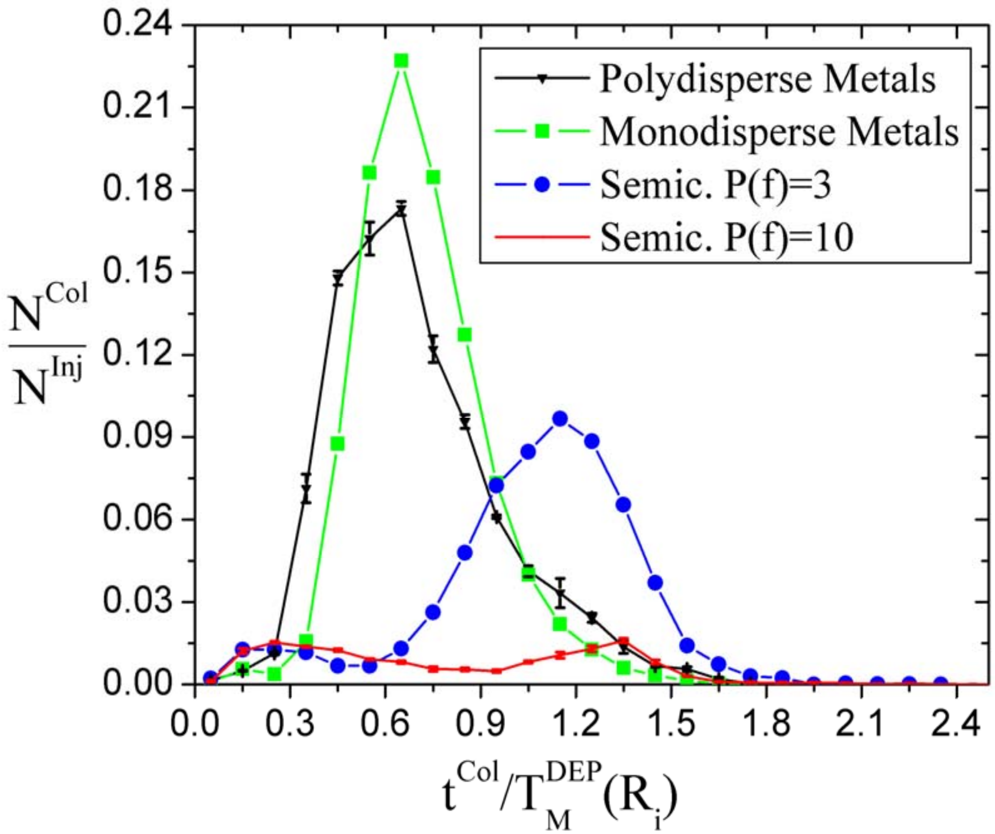


EFFECT OF ENSEMBLE SIZE: DEP + EP

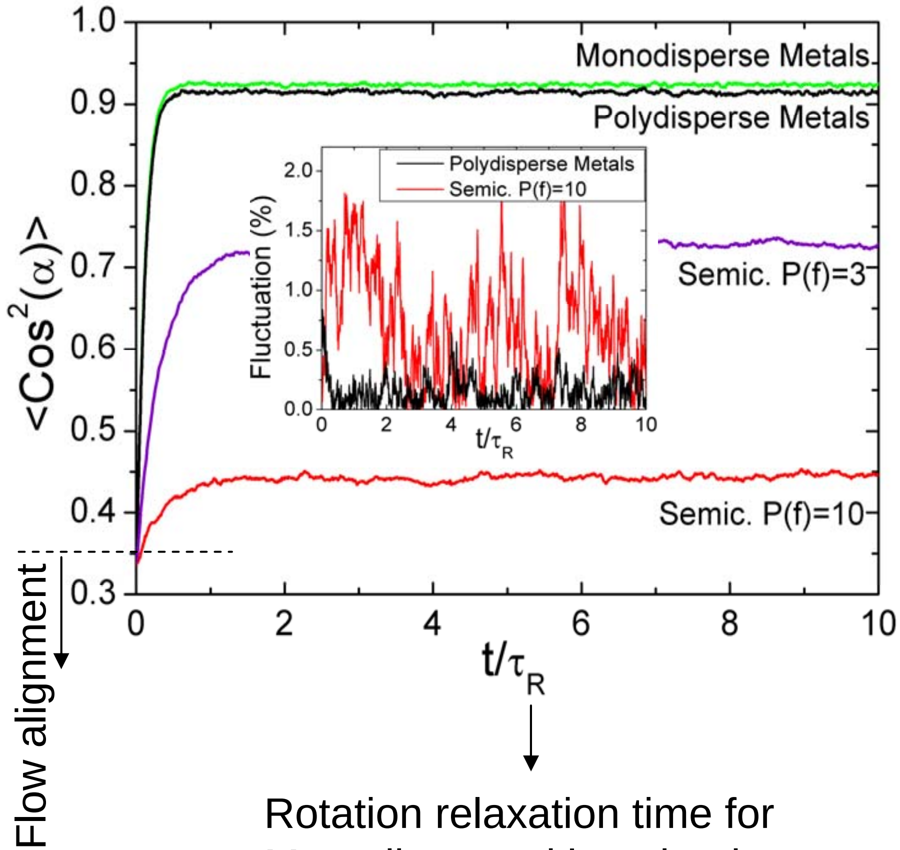
- Results with best Channel Length $L=54.2R_2$
- The small error values shown for Metals and Semiconductors w/ $S_{MS}=10$ in both plots indicate that the number of particles used is high enough



Histogram of Collected SWNTS



Average Orientation

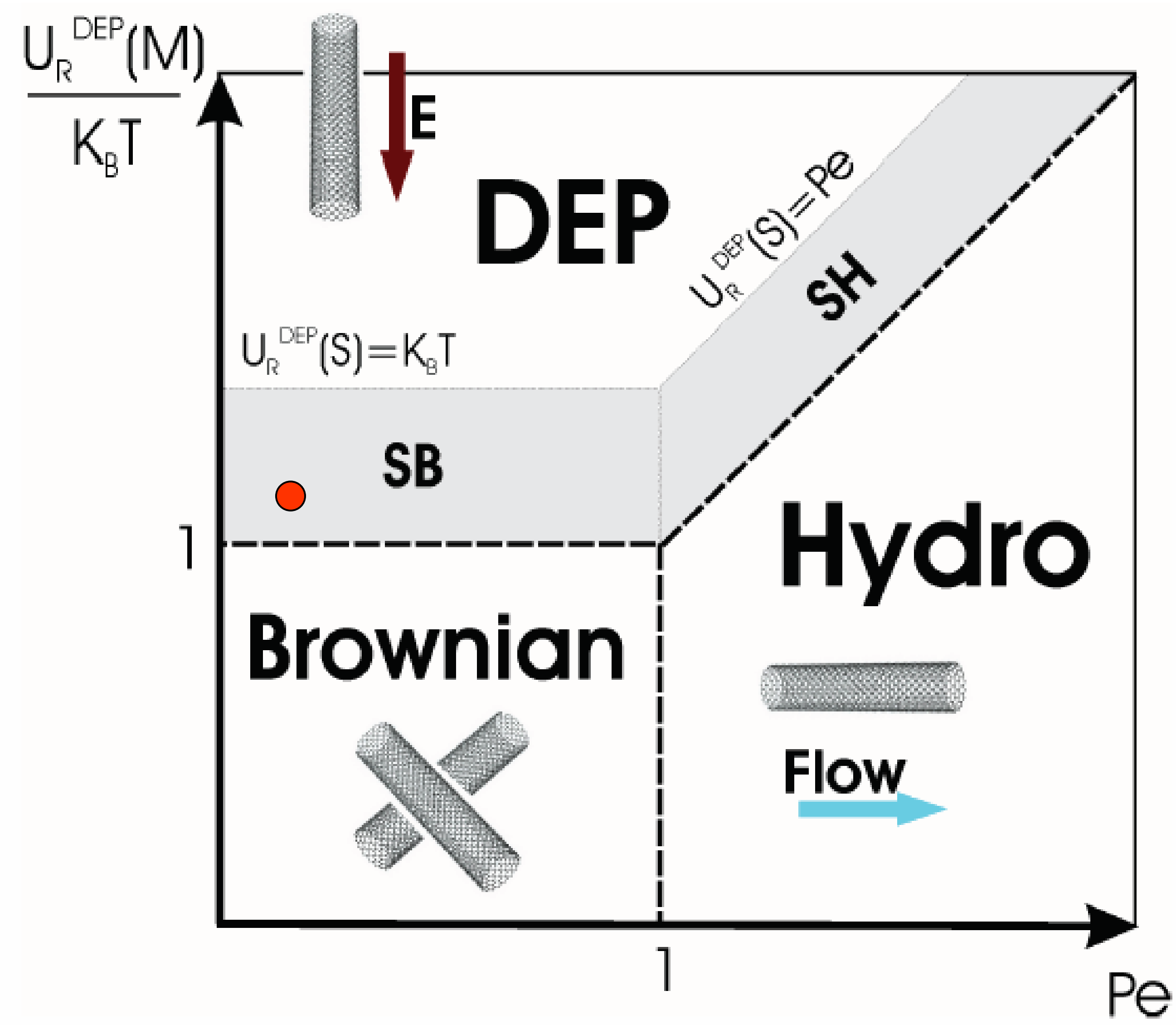


Rotation relaxation time for Monodispersed length tubes

PHASE DIAGRAM AND OPTIMIZATION

$0 = F^{DEP} + F^{Hydro} + F^{Brown}$

$0 = M^{DEP} + M^{Hydro} + M^{Brown}$

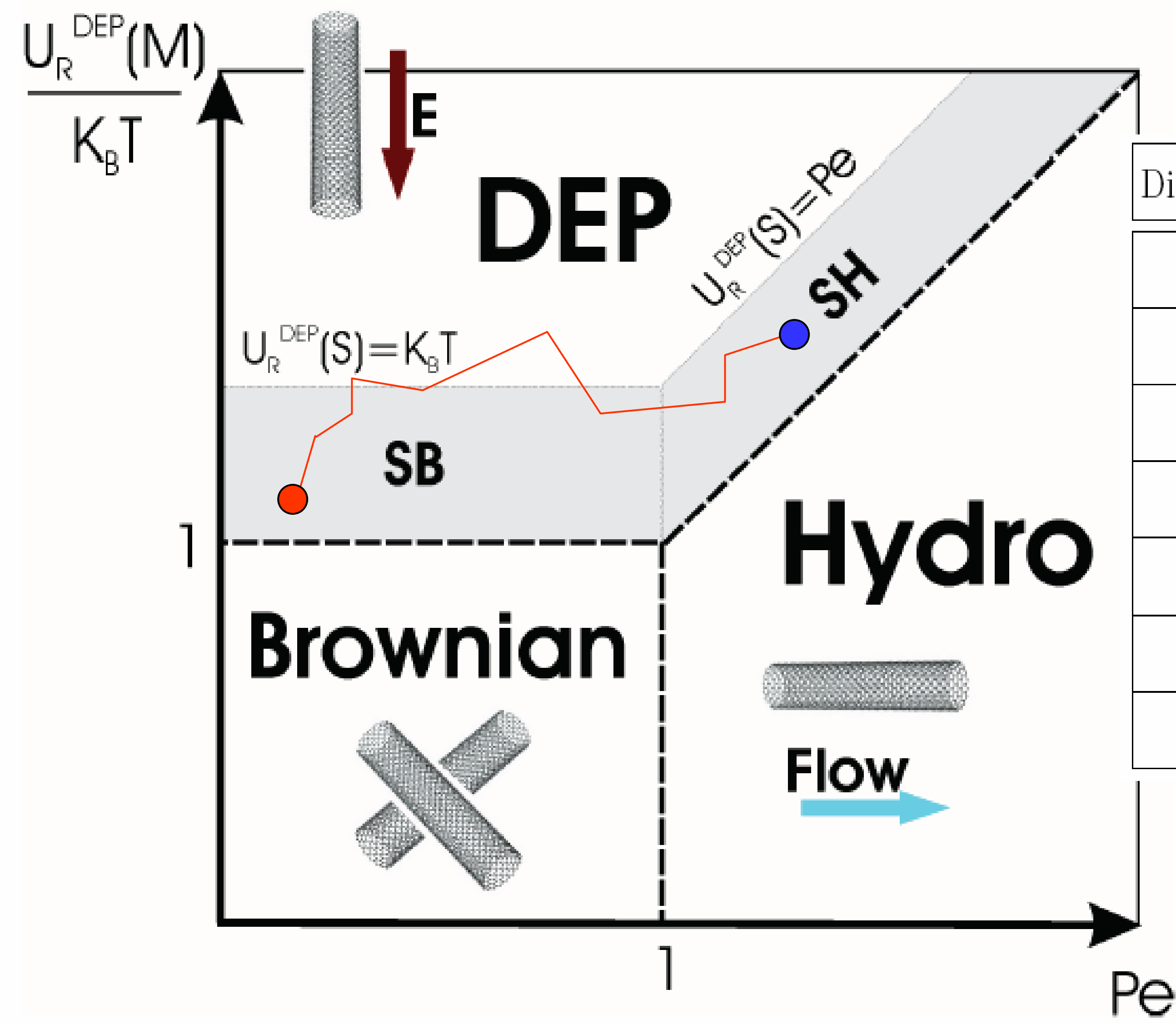


Optimal conditions obtained w/ a *Nelder and Mead direct search algorithm*. This iteratively searches for the <u>maximum in</u> **<u>separation performance</u>** as a function of the device parameters

PHASE DIAGRAM AND OPTIMIZATION

$$0 = F^{DEP} + F^{Hydro} + F^{Brown}$$

$$0 = M^{DEP} + M^{Hydro} + M^{Brown}$$



Dimensionless quantity	Optimized value
$\frac{R_2}{l_P}$	587.5
$\frac{U_R^{DEP}(M,R_2)}{K_BT}$	118.9
$\frac{T^{DEP}(R_2 \to R_1)}{T^{BM}(R_2 \to R_1)}$	9.42×10^{-3}
$Pe(R_1)$	18.13
$\frac{F_M^{DEP}(R_2)}{F^E(R_2)}$	10.9
L/R_2	4765.96
Performance	0.991

$$\frac{M_M^{DEP}(R_2)}{M^{Hydro}(R_2)} = 9.66$$

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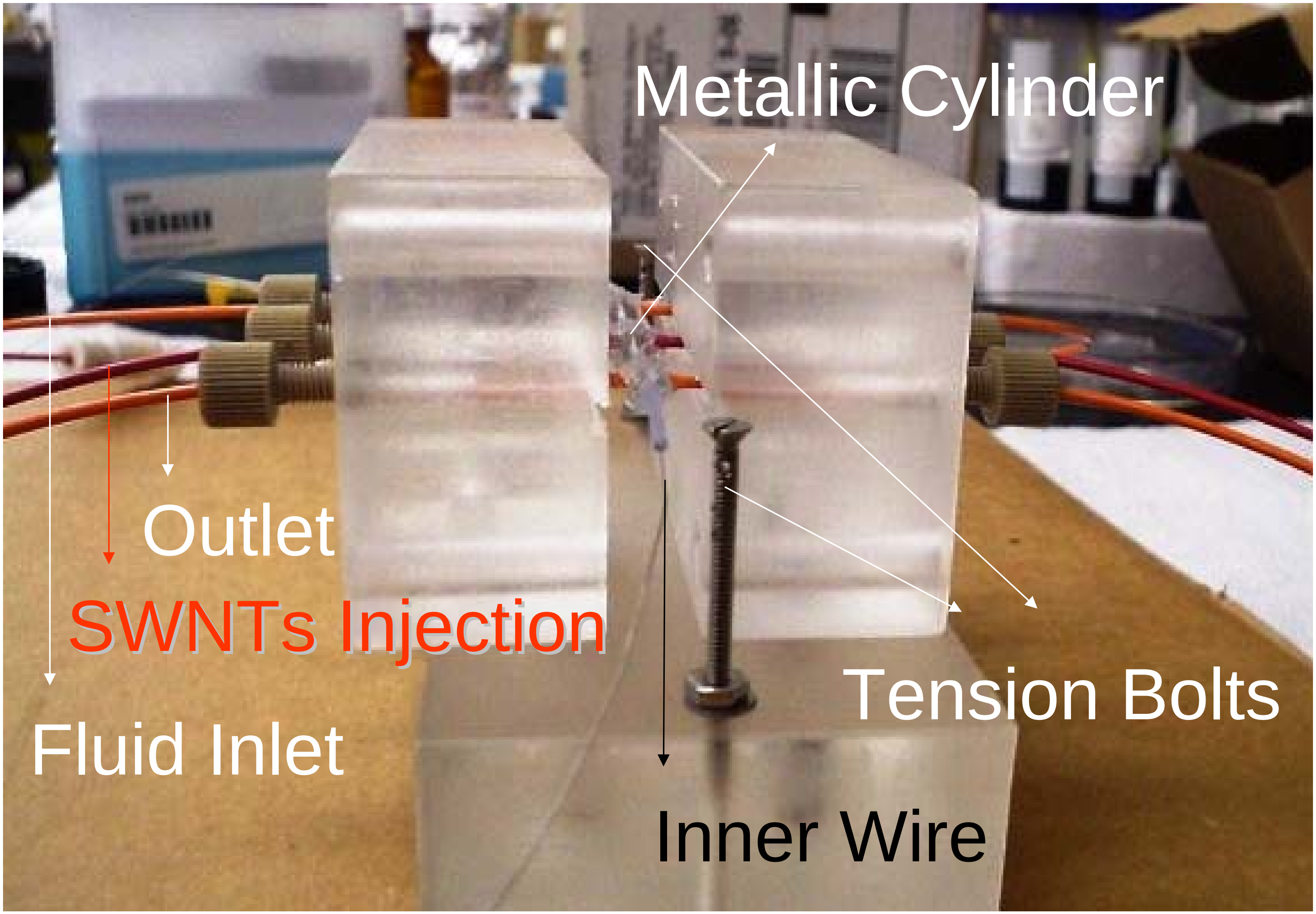
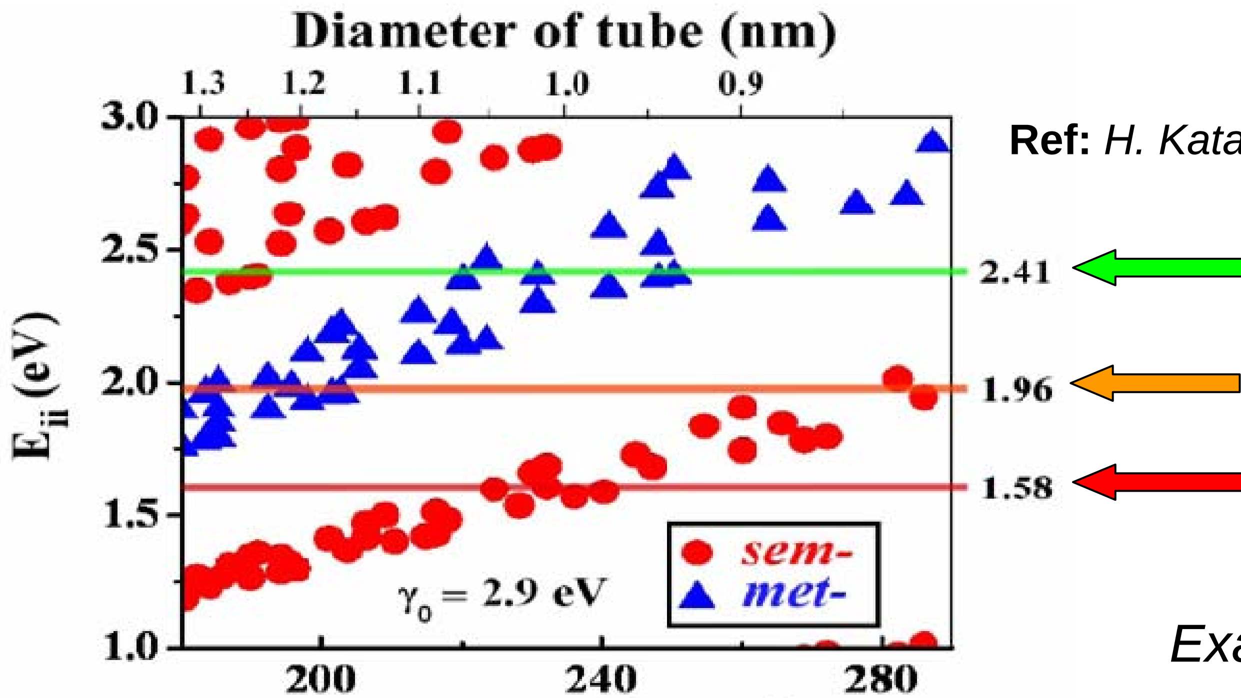
THE DEP SEPARATION DEVICE



MEASURING TYPE ENRICHMENT

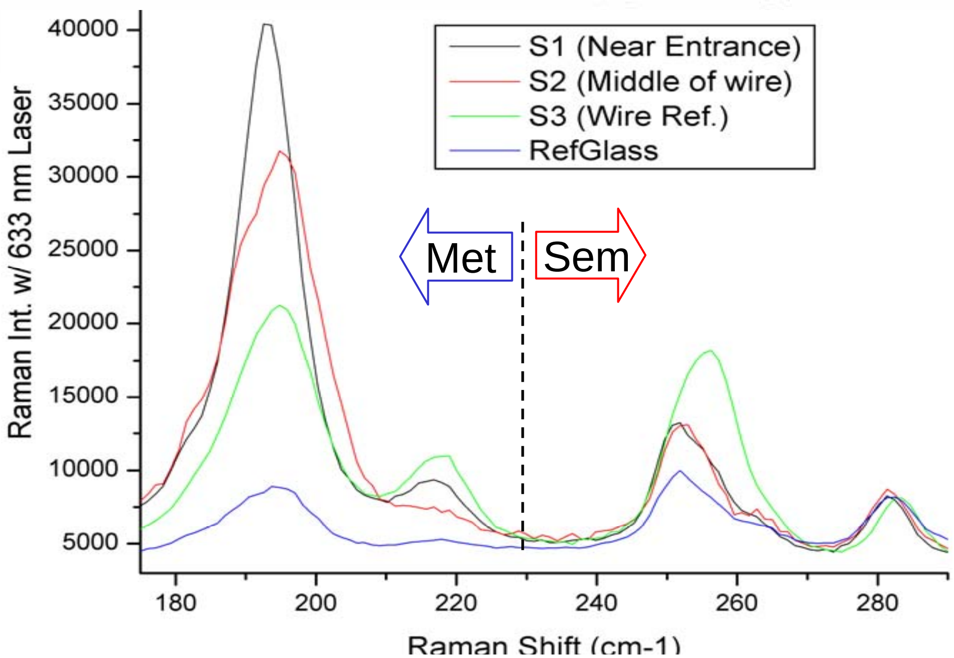


Ref: *H. Kataura et al.* Synthetic Metals, 1999

λ=514.5 nm

λ=633 nm

λ=785 nm



Example with <u>633 laser</u>:

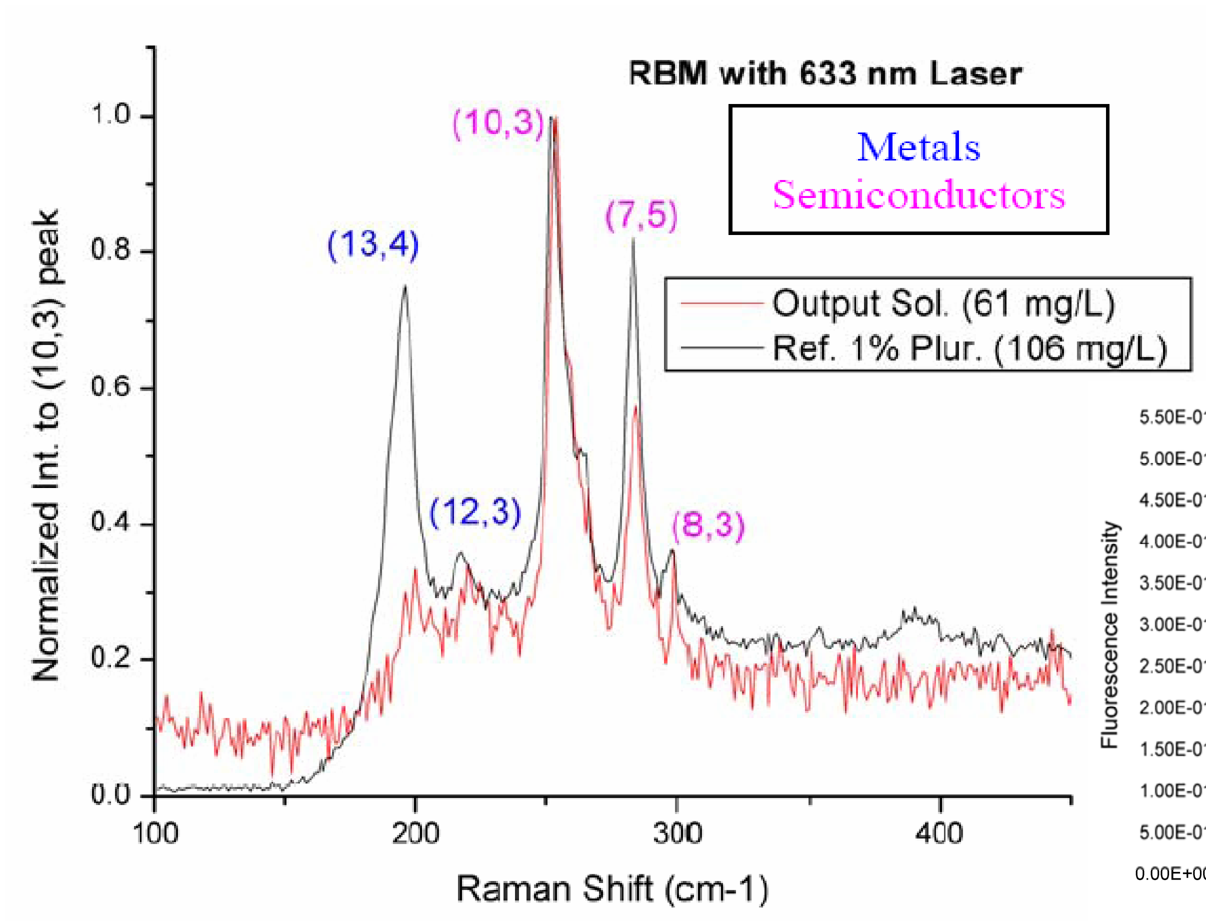
- The ***peaks relative intensity*** show that mostly Metallic tubes were collected at different spots along the wire

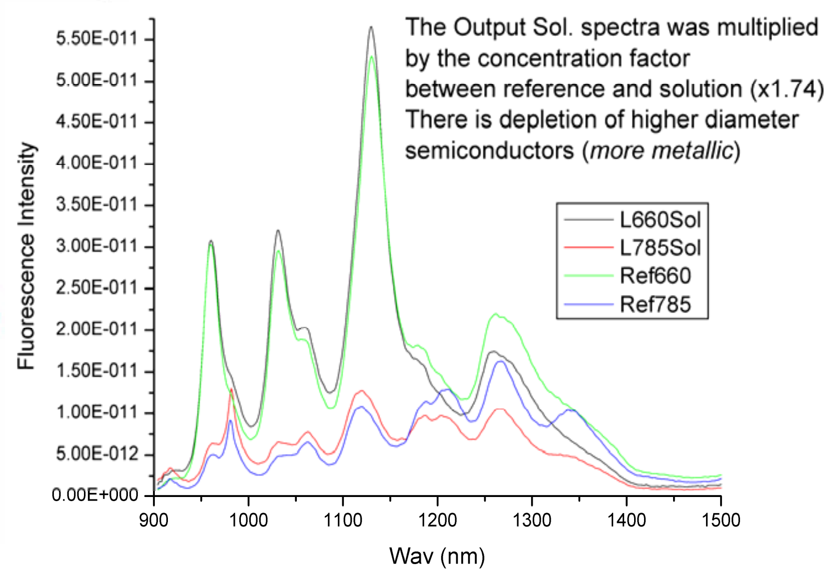
- Liquid Phase Raman is currently the most accurate method for measuring separation. *Solid phase can be troublesome*

OUTPUT SOLUTION ANALYSIS

- Simple test with a single flow using a 1% Pluronic (F108) decant
- <u>*F = 42 MHz*</u>

- Initial sol. Conc.= 106 mg/L
- Eluate conc.= 61 mg/L
- Eluate mostly has semiconductors
- ~ 40% SWNTs collected on wire

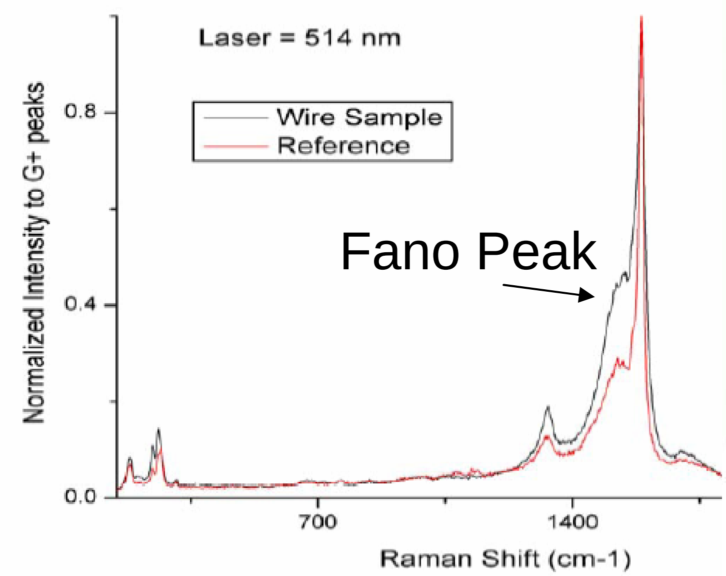


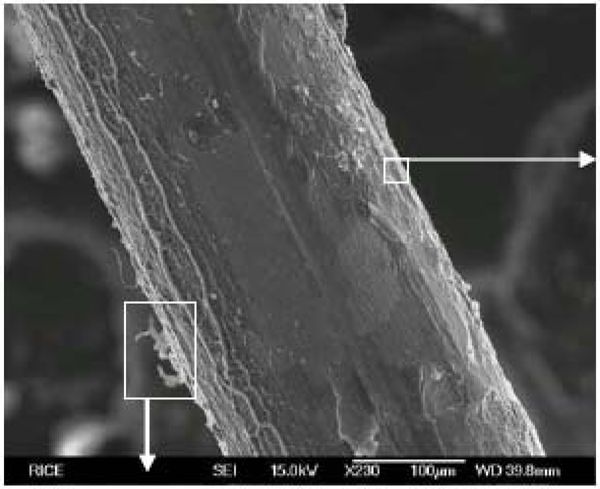


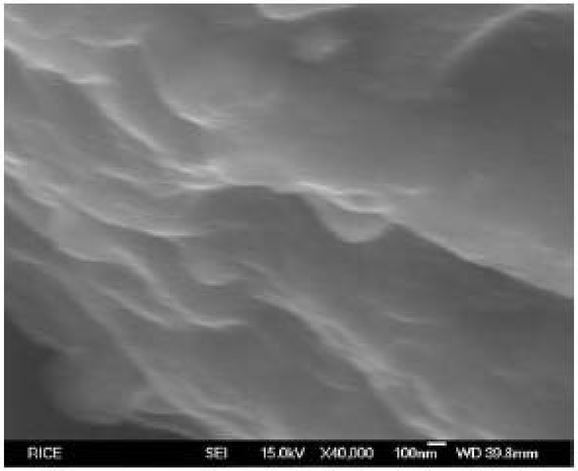
LOOKING AT THE WIRE

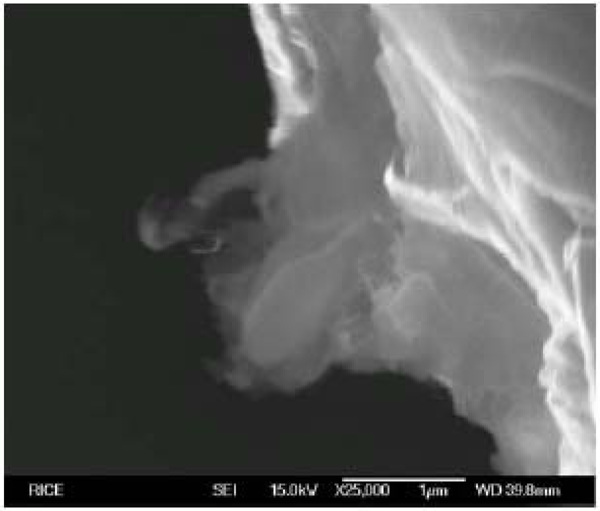
- The wire gets covered with a foam of SWNTs + surfactant with a density of ~ 20 mg/cm^2

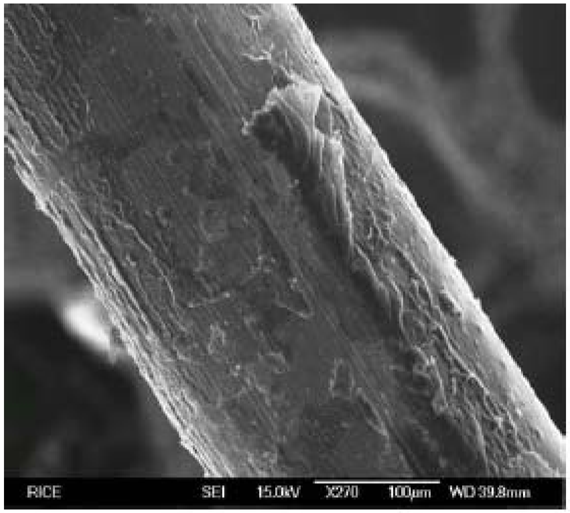
- The **Fano peak** relative increase in 514 Raman indicates metallic enrichment





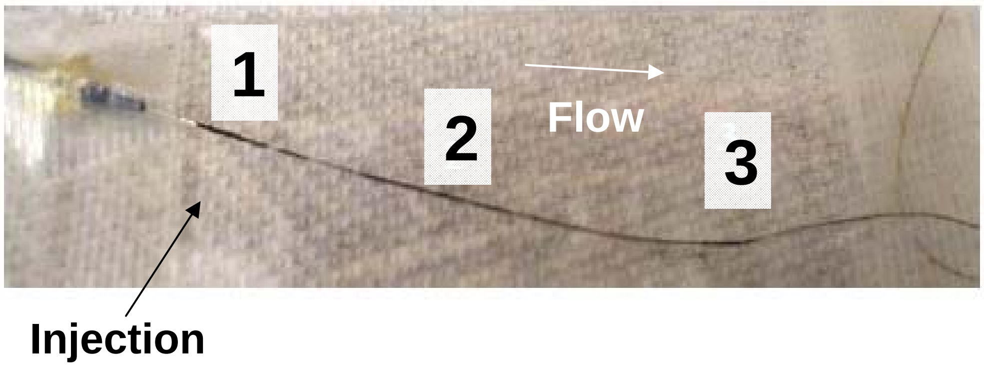


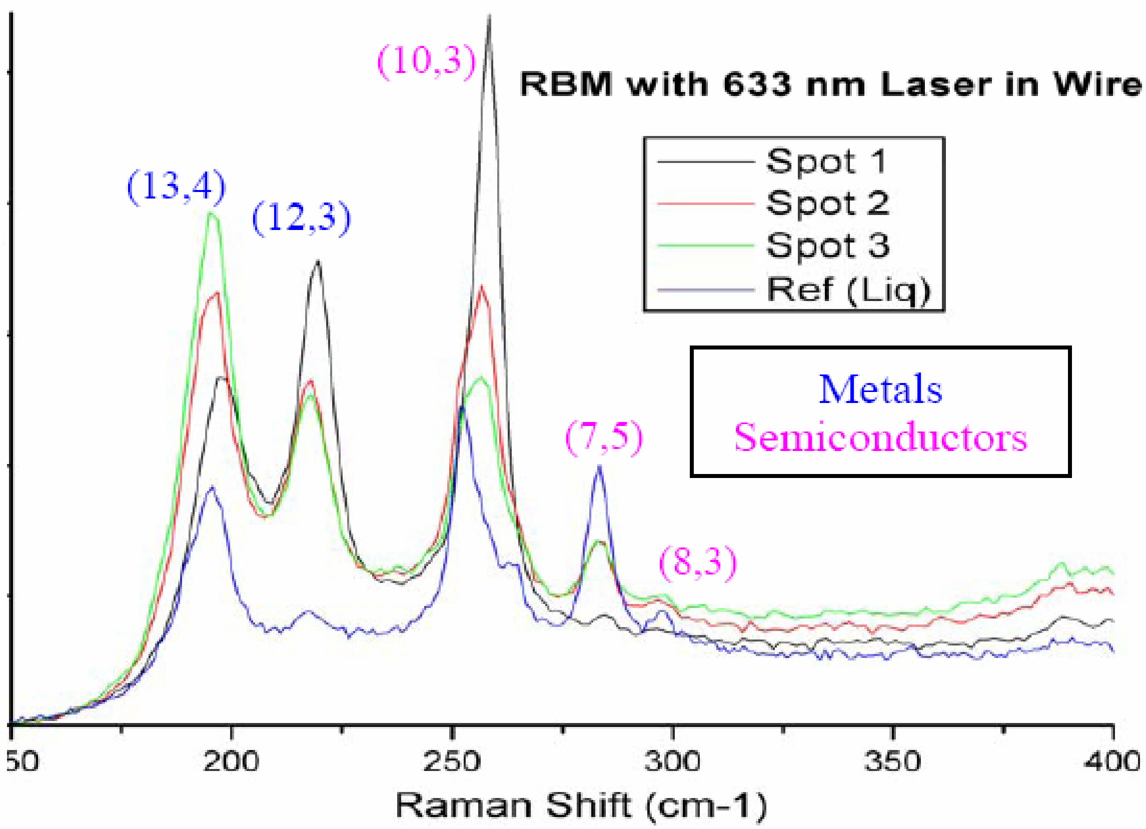




SEM by Laura McJilton

LOOKING AT THE WIRE





- Total Length = 50 mm
- Diameter = 0.254 mm

- Metallic enrichment can be measured by the *relative intensities of the (13,4) and (10,3) peaks* in 633 Raman

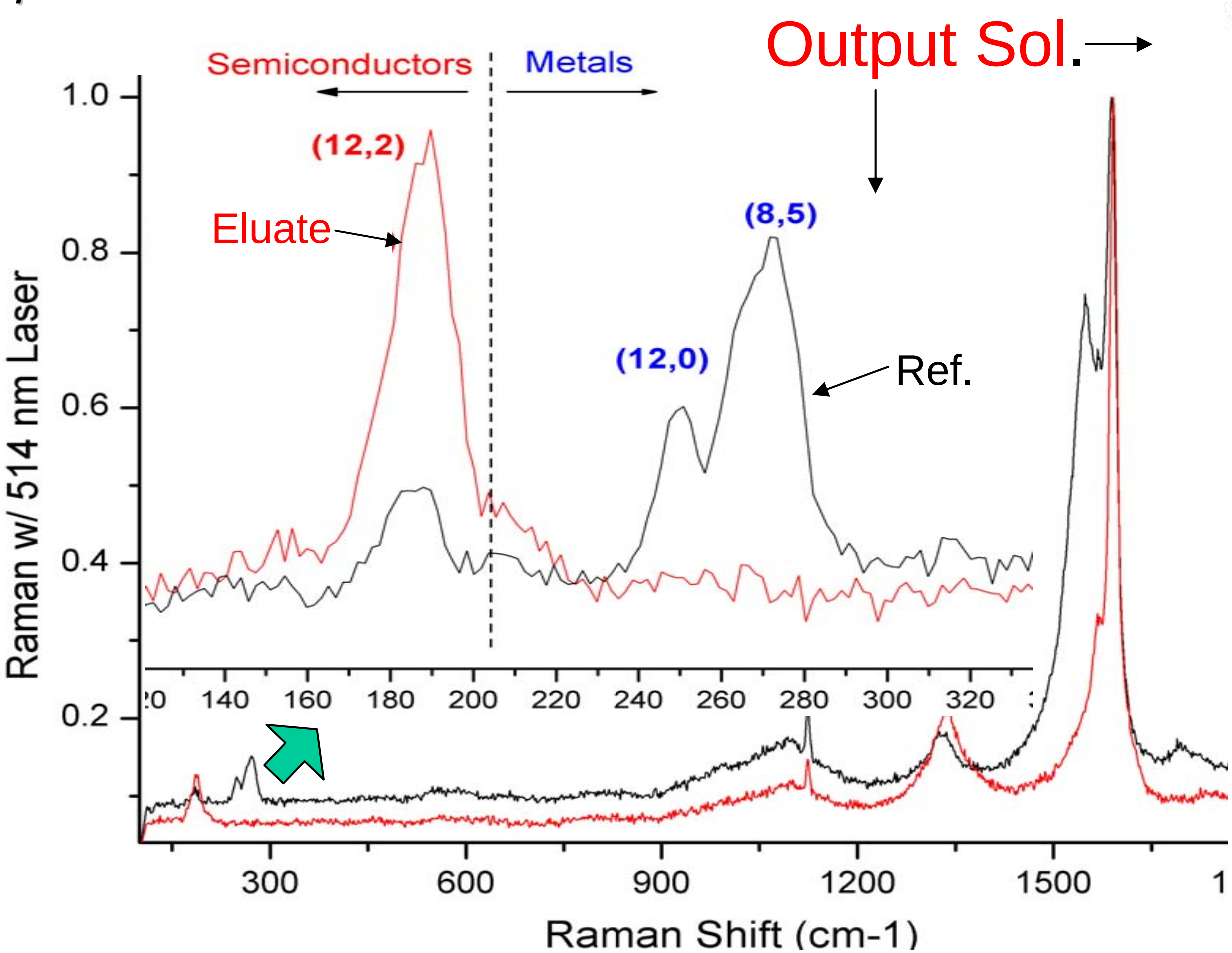
- Spot 1 is at the injection, so it collected a big agglomerate of all kinds of SWNTs (*taken as reference*)

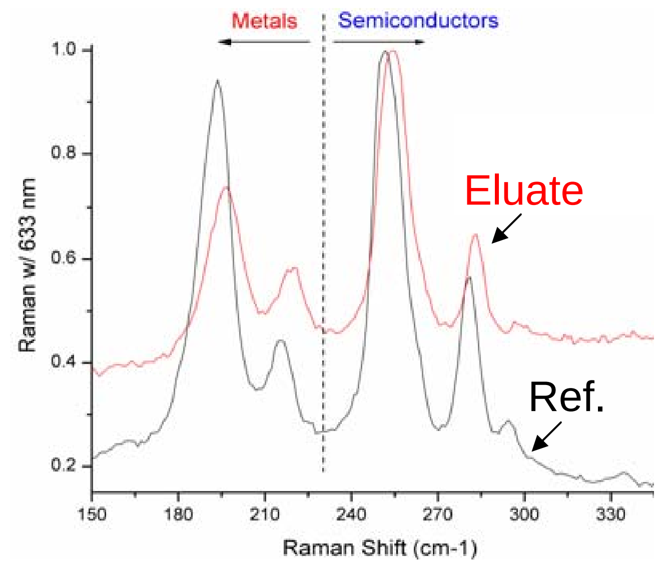
- **Spots 2 and 3** along the wire are metallic enriched

OUTPUT AND WIRE TESTS

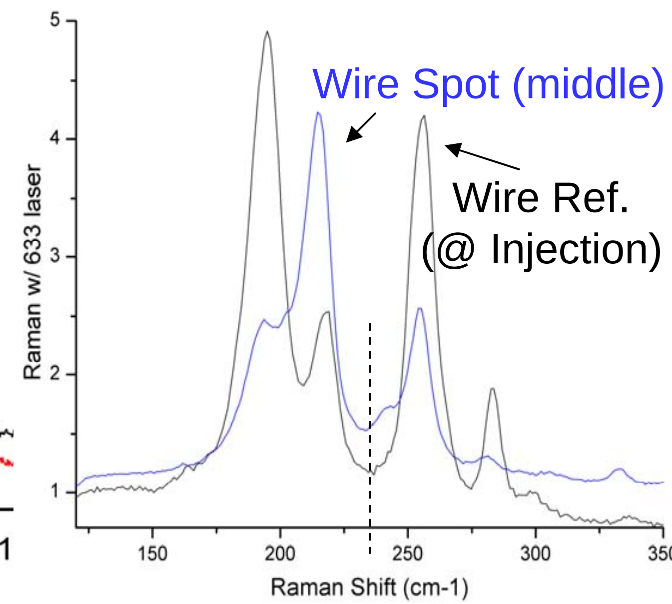
- Single solution flow (1% Pluronic) using smaller cylinder and wire dimensions. Significant enrichment measured with 514 laser

- <u>*F = 45 MHz*</u> – Both SWNT types appear to exhibit *positive DEP*



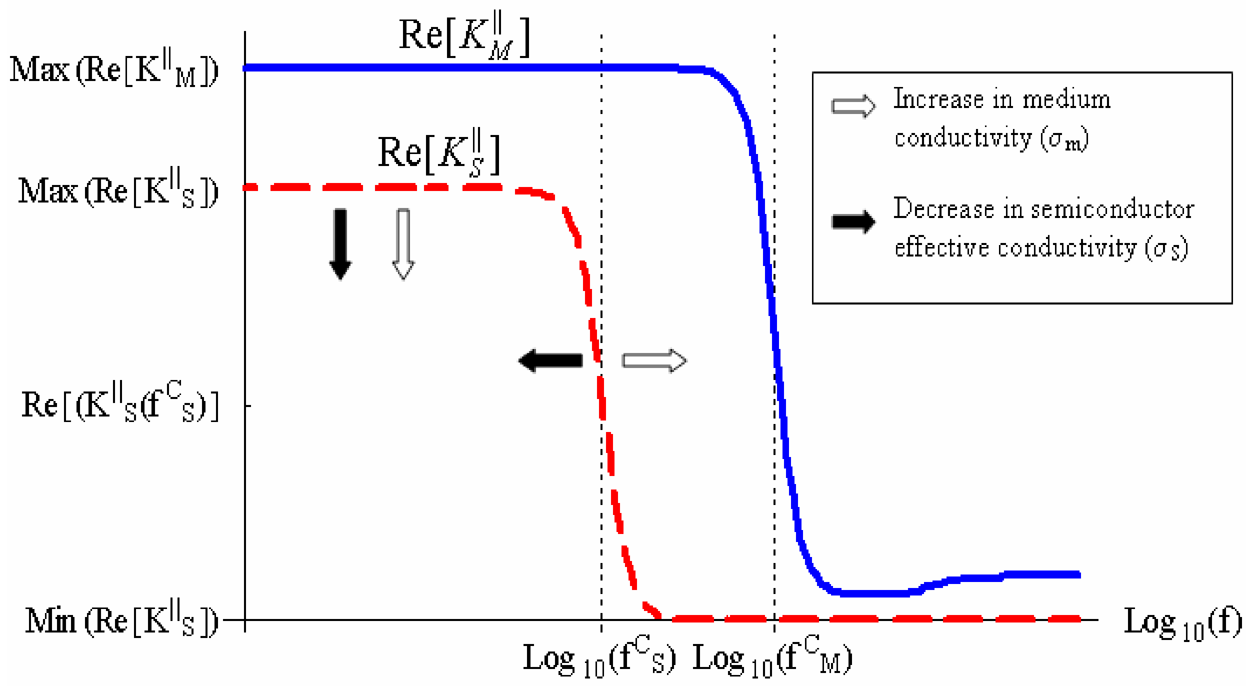


- **Wire** w/ 633 Raman:



STUDYING THE EFFECT OF SURFACTANT

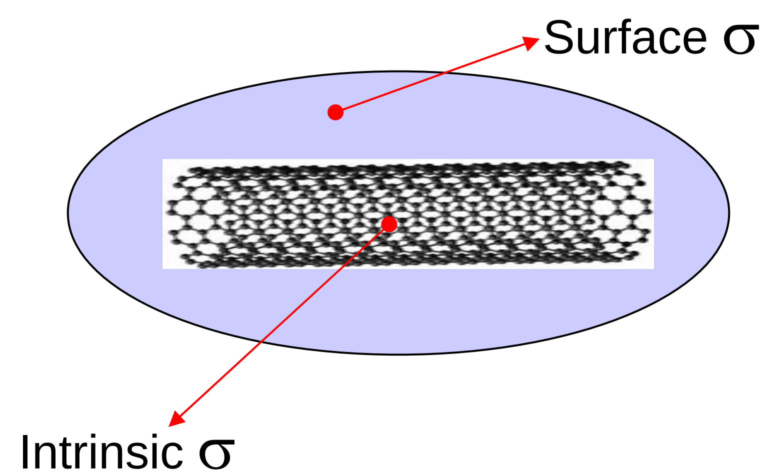
- The SWNT effective conductivity (**σ_{eff}**) - as seen by the medium - is the main physical property that enables type separation



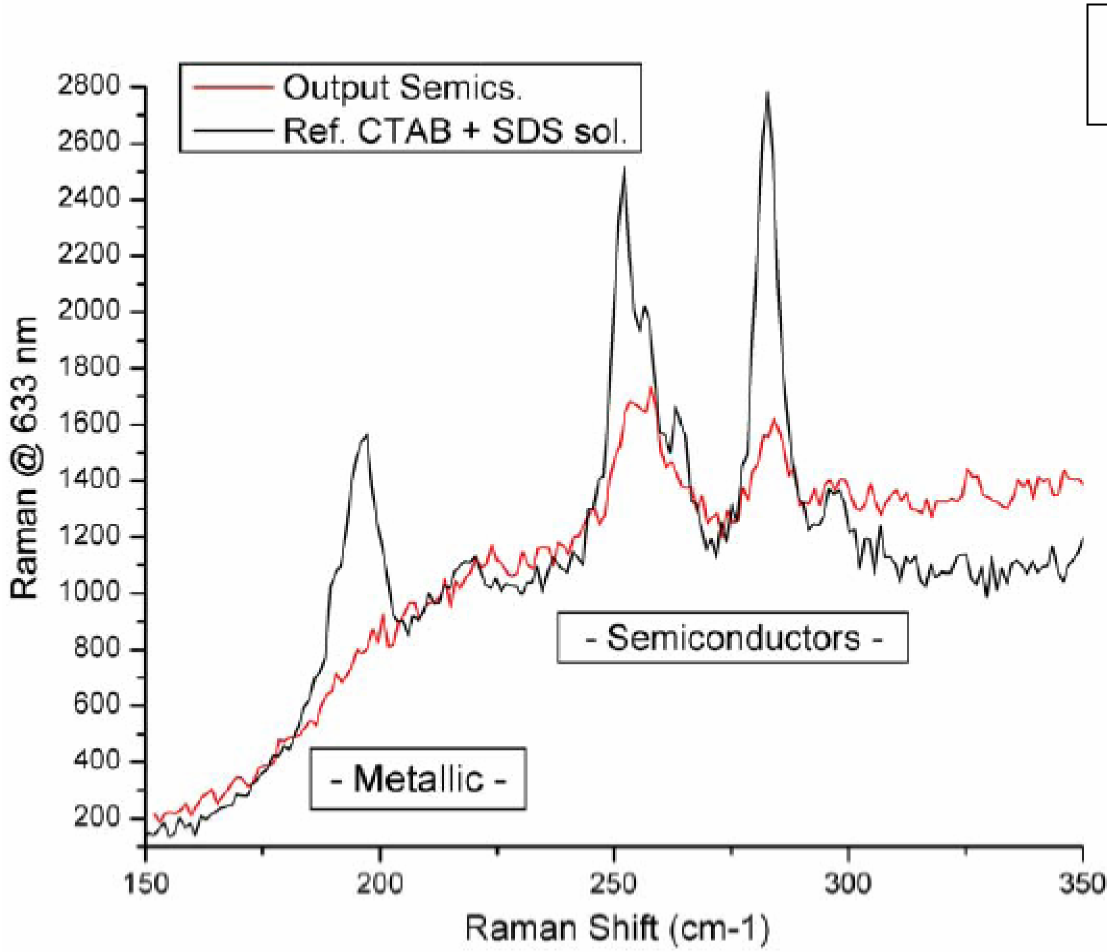
- This quantity is composed of two components:

$$\boxed{\sigma_{eff} = \boldsymbol{F}\ \textbf{\textit{(Surface}}\ \sigma, \textbf{\textit{Intrinsic}}\ \sigma\textbf{)}}$$

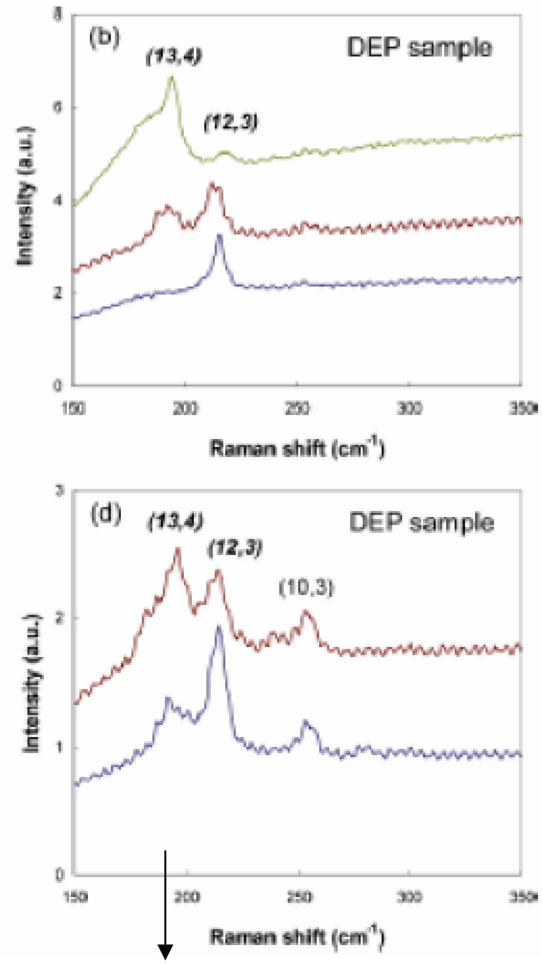
➢ It should be possible to tune $\boldsymbol{\sigma_{eff}}$ by changing the surfactant layer conductivity



COMPARISON WITH *STRANO et al.* WORK USING A CTAB+SDS EQUIMOLAR MIXTURE



Results from Strano paper for Metallic SWNTs deposited on the electrodes



(d) Smaller number of electrodes

- Total Metallic depletion was achieved by using a <u>combination of 2 surfactants</u>: SDS(-) in CTAB(+) SWNT solution with equimolar ratio (1:1)
- SWNTs flocculated due to heating

Ref: *Kim et al.* J. Phys. Chem. B, 2006

CONCLUSIONS

- Model is in **dimensionless variables**; can be converted into dimensional parameters once the properties of liquid, surfactant, and SWNTs (metallic & semiconducting) are determined
- A **99.1% sorting performance** can be achieved at optimal conditions if:
  - No short tubes (below ~250 nm) are present and the length distribution is narrow (standard deviation ~ 78 nm). This can be obtained using length sorted or carpet grown SWNTs.
  - The **polarization ratio P(f)** is 10 or higher (at least one order of magnitude difference between the DEP force on metals and the one on semiconductors)
- Experimental tests show good separation at a frequency of **45 MHz** either by:
  - Using a **non-ionic** surfactant (Pluoronic F108)
  - Or an equimolar **mixture of a Cationic and Anionic** surfactant (CTAB:SDS)
- Once optimal surfactant is determined, we will adapt the device to operate at the simulation conditions to approach the predicted optimal performance
- Performing <u>sequential runs</u> with solutions of just semiconductors may yield specific (n,m) chirality enrichment

ACKNOWLEDGEMENTS

- **Funding:** NASA under HARC Grant: NNJ06HI25A / ETF Grant: 07082301

- **Co-authors:**
  - Manuel Mendes
  - Noe Alvarez
  - Howard Schmidt

- **CNL Members:**
  - Prof. James Tour
  - Prof. Robert Hauge
  - Carter Kittrel

- **Special Thanks:**
  - Nikhil Sheakar
  - Dvir Kafri
  - Haiqing Peng
  - Juan Duque
  - Laura McJilton
  - Nick Parra-Vazquez
  - Neeraj Rohilla
  - Paul Cherukuri

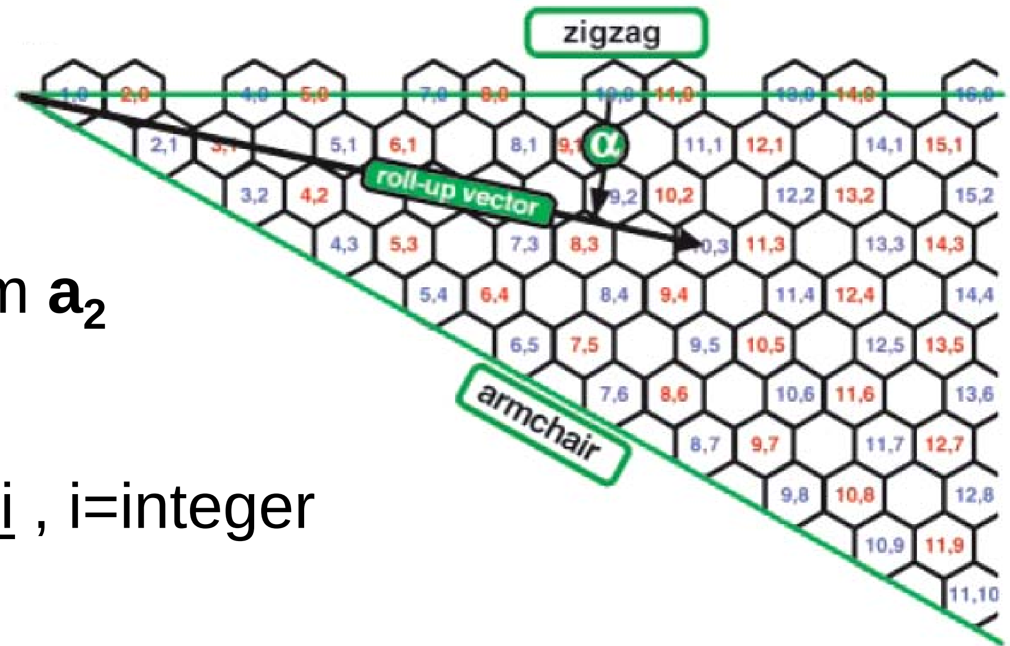
Howard Schmidt

Manuel J. Mendes

Noe Alvarez

Backup Slides

SWNT STRUCTURE AND TYPES



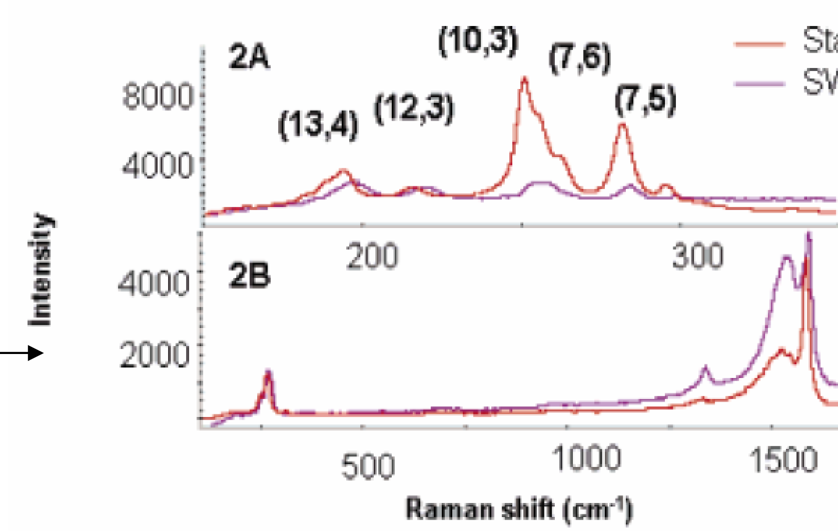
- Chiral vector: $\mathbf{C_h} = n\,\mathbf{a_1} + m\,\mathbf{a_2}$
- Metallic tubes have <u>n-m=3i</u> , i=integer
- As produced HipCo SWNTs exhibit > 50 (n,m) chiralities
- Equidistribution of Chiralities: *1/3 are metallic tubes and 2/3 are semiconductors*

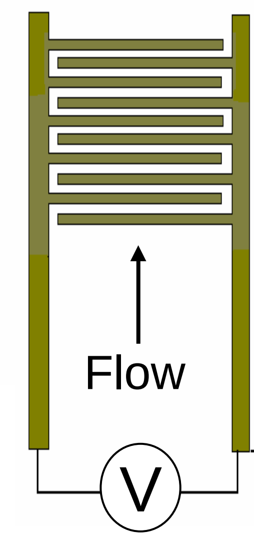
Ref: *Bachilo et al.* Science, 2002

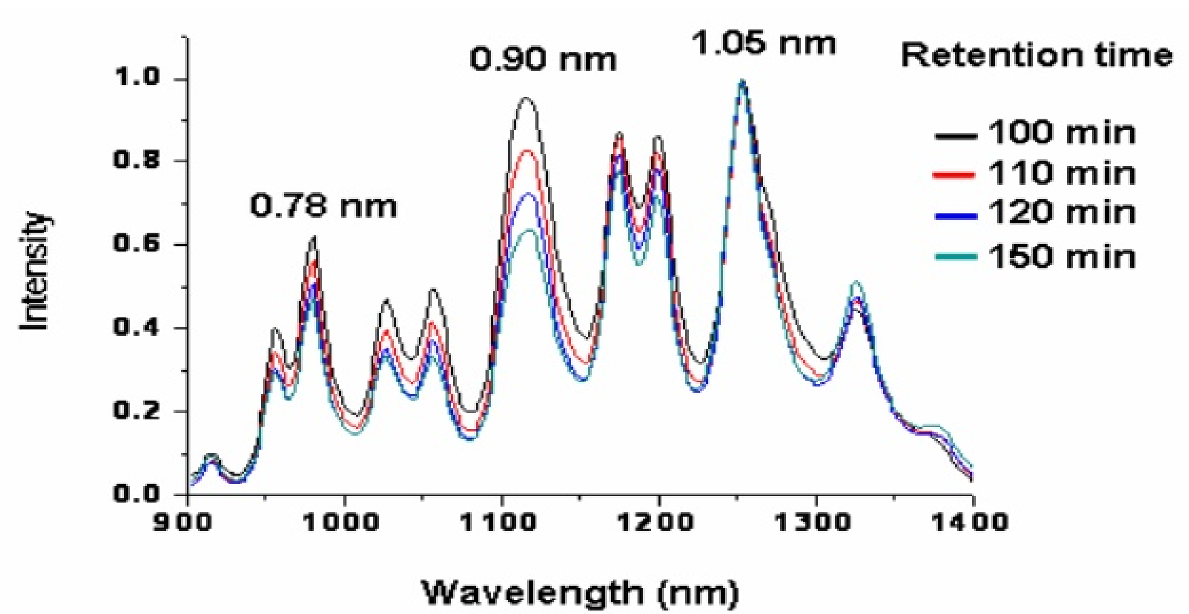
DIELECTROPHORESIS SO FAR AT RICE

- Bottom of the chamber filled with a Au gold array of 2x50μm electrodes with a 50μm spacing

- Raman spectra collected with a 633 nm (A) and a 514 nm (B) laser excitation







- **70% type enrichment** achieved with DEP-Field Flow Fractionation (FFF)

Ref: *Haiqing Peng et al.* JACS, 2006

CLAUSIUS-MOSSOTTI FACTOR

- Known Values:
  - $\varepsilon_S = 5\ \varepsilon_0$
  - $\varepsilon_M = 10^4\ \varepsilon_0$
  - $\varepsilon_m = 80\ \varepsilon_0$
  - $-\ \sigma_m = 10^{-3}$ S/m

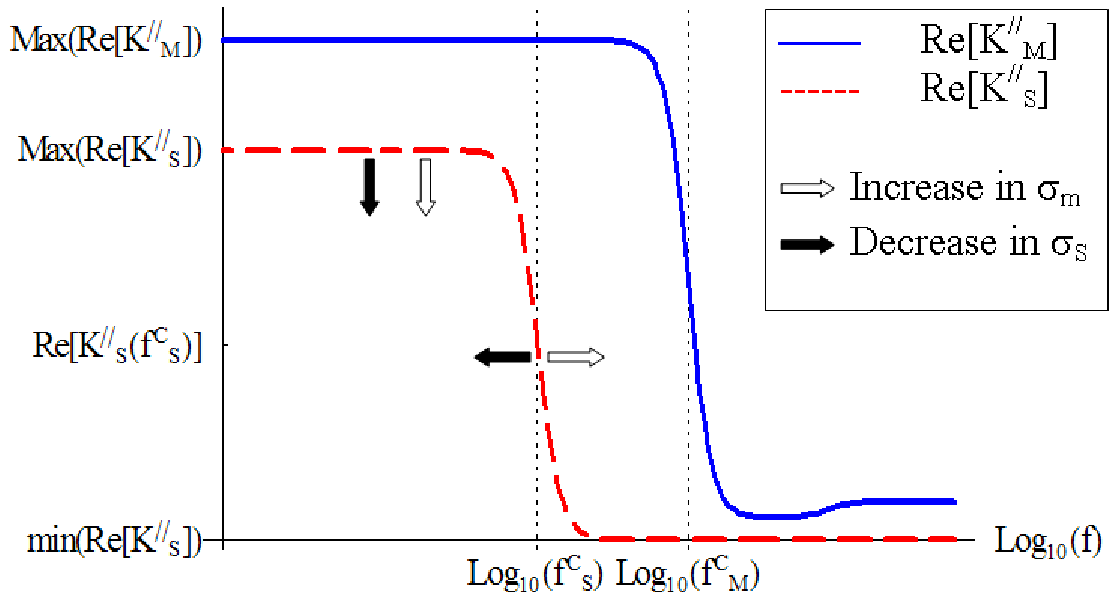
$$\mathbf{F}^{DEP} = \frac{V_{NT}}{2}\epsilon_m Re\left[K\right]\nabla E^2$$

$$\boxed{K^{\perp,//} = \frac{\epsilon^*_{NT} - \epsilon^*_m}{\epsilon^*_{NT} + (\epsilon^*_{NT} - \epsilon^*_m)L^{\perp,//}}} \quad \epsilon^* = \epsilon - i\frac{\sigma}{2\pi f}$$

- Estimated values:
  - f_S^c = 1Mhz : $\sigma_S = 10^2$ S/m
  - $f \sim f_S^c$: $Re[K_M] = Max(Re[K_M])$
    $\sigma_M = 10^5$ S/m

- Results will only be function of the **separation ratio** set by changing f around f_S^c

$$\boxed{S_{MS} = \frac{Re\left[K^{//}_M\right]}{Re\left[K^{//}_S\right]}}$$



Effect of Surfactants on SWNTs K factor

Ref: *Ralph Krupke et al.* Nano Lett., 2004

MIXTURES OF ANIONIC (-) AND CATIONIC (+) SURFACTANTS

- *Objective:* Reduce the SWNT Surface σ to achieve better separation performance at the MHz range

- Anionic and Cationic mixtures don't have good stability when heated up to 80-100 ^{o}C

- Different mixtures were tried with several volume ratios using:
  - NaCh (-)
  - CTAB (+)
  - SDBS (-)
  - SDS (-)

- The combinations that showed best stability under heating are displayed on the graph